

PATENT APPLICATION

**TITLE: HIGH STABILITY, HIGH LUBRICITY, LOW TOXICITY, HIGH
BIODEGRADABILITY DRILLING FLUID**

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HIGH STABILITY, HIGH LUBRICITY, LOW TOXICITY,
HIGH BIODEGRADABILITY DRILLING FLUID

CROSS REFERENCE TO RELATED APPLICATIONS

[1] This application claims priority to U.S. Provisional Application Serial No. 60/449,557, filed on February 24, 2003.

FEDERALLY SPONSORED RESEARCH

[2] Not applicable.

REFERENCE TO MICROFICHE APPENDIX

[3] Not applicable.

FIELD OF THE INVENTION

[4] The present invention relates to drilling fluids derived from the products of a Fischer-Tropsch synthesis. More particularly, the invention relates to base fluids, and drilling fluids produced therefrom, having high stability, lubricity, and biodegradability while also having low toxicity. The invention further relates to processes of producing and using the drilling fluids.

BACKGROUND OF THE INVENTION

[5] Drilling fluids, or drilling muds, are well known for use in oil and gas well drilling operations. In early applications, crude, diesel and mineral oils were used as base fluids in formulating drilling fluids. Such oil based drilling fluids, however, have unacceptable toxicity and persistence, or non-biodegradability. Toxicity and persistence issues are especially critical in offshore drilling operations. Pseudo-oil based drilling fluids are also well known wherein the base fluids are fatty acid esters or synthetic hydrocarbons. Such synthetic hydrocarbons have included polyalphaolefins, linear alphaolefins, internal olefins, and mixtures thereof as well as linear and branched paraffins and mixtures thereof. Synthetic olefinic and paraffinic base fluids produced by oligomerizing low carbon number hydrocarbons are well known but are expensive to produce. Similarly, ester base fluids are expensive to produce.

[6] The cost of drilling fluids may be reduced by use of Fisher-Tropsch synthesis to produce paraffinic base fluids. Paraffinic drilling fluids, however, generally do not have adequate low temperature properties for use in offshore and cold weather drilling operations.

[7] One approach to the low temperature issue incorporates multi-methyl branched isoparaffins or isoparaffins with branches of higher carbon number than methyl into the paraffinic base fluid. Such paraffinic base fluids contain C₁₀-C₂₄ n-paraffins and isoparaffins, with an iso to normal ratio ranging from 0.5:1 to 9:1. Greater than 50% of the total isoparaffin content are mono-methyl branched isoparaffins and about 30% are multi-methyl substituted. A similar approach to the low temperature issue involves formulation of a drilling fluid containing a mixture of n-paraffins and isoparaffins wherein at least 90% of the isoparaffins are mono- or poly-methyl branched isomers. Although the use of Fisher-Tropsch synthesis somewhat lowers the cost of such paraffinic drilling fluids, the necessity of hydrocracking and hydroisomerization adds to the overall cost of the drilling fluid. Moreover, to sufficiently improve the low temperature properties of the paraffinic base fluids, pour point depressant additives may be required, further increasing the cost of the drilling fluid.

[8] In another known drilling fluid a base fluid of a mixture of linear and branched alphaolefins with the linear to branch ratio ranging from 1:1 to 5:1 is used. In this known drilling fluid the olefins may be produced from high temperature Fischer-Tropsch synthesis. High temperature Fischer-Tropsch synthesis, however, results in primarily internal branching of the branched hydrocarbons. Thus, such drilling fluids are not wholly biodegradable resulting in increased persistence. Moreover, because of the reactivity of olefins, drilling fluids composed of olefins are easily oxidizable and, therefore, must be stored under a nitrogen blanket to provide a reasonable shelf life. Even with nitrogen padding, olefinic drilling fluids cannot be stored for periods as long as paraffinic drilling fluids. Therefore, the cost of using olefinic drilling fluids is increased by both its special storage requirements and loss of oxidized product.

[9] Therefore, there remains a need for a further improved lower cost drilling fluid having oxidative stability, high lubricity, low toxicity, improved low temperature properties, and high biodegradability.

SUMMARY OF THE INVENTION

[10] In one embodiment of the invention, a base fluid which may be used for drilling fluid
5 formulation is provided. The base fluid includes at least about 5 wt% olefins, at least about 5
wt% n-paraffins and between about 2 and 50 wt% branched paraffins wherein substantially all
of the branch groups are monomethyl and wherein the ratio of terminal monomethyl branching
to internal monomethyl branching is at least about 1:1.5.

[11] In other embodiments of the invention a drilling fluid is provided wherein the drilling
10 fluid contains between about 2 and about 90 wt% olefins, between about 5 and about 90 wt% n-
paraffins and between about 0 and about 10 wt% oxygenates.

[12] Yet another embodiment of the invention provides a process for producing a drilling
from a light Fischer-Tropsch liquid.

BRIEF DESCRIPTION OF THE DRAWINGS

[13] None.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[14] The term " C_x ", where x is a number greater than zero, refers to a hydrocarbon compound
20 having predominantly a carbon number of x. As used herein, the term C_x may be modified by
reference to a particular species of hydrocarbons, such as, for example, C_5 olefins. In such
instance, the term means an olefin stream comprised predominantly of pentenes but which may
25 have impurity amounts, i.e. less than about 10%, of olefins having other carbon numbers such
as hexene, heptene, propene, or butene. Similarly, the term " C_{x+} " refers to a stream wherein the
hydrocarbons are predominantly those having a hydrocarbon number of x or greater but which
may also contain impurity levels of hydrocarbons having a carbon number of less than x. For
example, the term C_{15+} means hydrocarbons having a carbon number of 15 or greater but which
30 may contain impurity levels of hydrocarbons having carbon numbers of less than 15. The term
" C_x-C_y ", where x and y are numbers greater than zero, refers to a mixture of hydrocarbon
compounds wherein the predominant component hydrocarbons, collectively about 90% or
greater by weight, have carbon numbers between x and y inclusive. For example, the term C_5-
 C_9 hydrocarbons means a mixture of hydrocarbon compounds which is predominantly

comprised of hydrocarbons having carbon numbers between 5 and 9 inclusive, but may also include impurity level quantities of hydrocarbons having other carbon numbers.

[15] As used herein the term "high lubricity" means having a wear scar of average diameter of about ≤ 0.46 mm at 60°C tested in accordance with ASTM Standard D-6079-02 entitled "Standard Test Method for Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig." The terms "high stability" and "high oxidative stability" mean having a total solids ≤ 1.5 mg/100 ml tested in accordance with ASTM Standard D-22-74-01a entitled "Standard Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)."

Note that these methods are being applied herein to the analysis and characterization of synthetic products although the standards refer expressly to petroleum derived products.

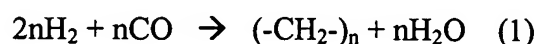
[16] Unless otherwise specified, all quantities, percentages and ratios herein are by weight.

[17] Embodiments of the drilling fluid of the invention contain a base fluid having from about 5 to about 90wt% linear alpha- and internal olefins, from about 5 to about 20wt% isoparaffins, from about 5 to about 90wt% n-paraffins and from about 0 to about 10wt% oxygenates. To fully realize the lower cost potential of the invention, the base fluid for the drilling fluid of such embodiments may be obtained from a Fischer-Tropsch synthesis using synthesis gas as a feed stock. Moreover, production of the drilling fluid from a base fluid produced by the Fischer-Tropsch synthesis and subsequent processing as described herein is desirable as it results in a product having the desirable olefin and paraffin contents. However, the base fluid composition may be otherwise produced while yet retaining the remaining advantages of the invention. Thus, some embodiments of the base and drilling fluids of the invention are not produced by Fischer-Tropsch synthesis.

[18] Three basic techniques may be employed for producing a synthesis gas, or syngas, which is used as the starting material of a Fischer-Tropsch reaction. These include oxidation, reforming and autothermal reforming. As an example, a Fischer-Tropsch conversion system for converting hydrocarbon gases to liquid or solid hydrocarbon products using autothermal reforming includes a synthesis gas unit, which includes a synthesis gas reactor in the form of an autothermal reforming reactor (ATR) containing a reforming catalyst, such as a nickel-containing catalyst. A stream of light hydrocarbons to be converted, which may include natural gas, is introduced into the reactor along with oxygen (O_2). The oxygen may be provided from compressed air or other compressed oxygen-containing gas, or may be a pure oxygen stream.

The ATR reaction may be adiabatic, with no heat being added or removed from the reactor other than from the feeds and the heat of reaction. The reaction is carried out under sub-stoichiometric conditions whereby the oxygen/steam/gas mixture is converted to syngas. Examples of Fischer-Tropsch systems are described in U.S. Patent Nos. 4,973,453; 5,733,941; 5,861,441; 6,130,259, 6,169,120 and 6,172,124, the disclosures of which are herein incorporated by reference.

[19] The Fischer-Tropsch reaction for converting syngas, which is composed primarily of carbon monoxide (CO) and hydrogen gas (H₂) may be characterized by the following general reaction:



[20] Non-reactive components, such as nitrogen, may also be included or mixed with the syngas. This may occur in those instances where air or some other non-pure oxygen source is used during the syngas formation.

[21] The syngas is delivered to a synthesis unit, which includes a Fischer-Tropsch reactor (FTR) containing a Fischer-Tropsch catalyst. Numerous Fischer-Tropsch catalysts may be used in carrying out the reaction. These include cobalt, iron, ruthenium as well as other Group VIIIB transition metals or combinations of such metals, to prepare both saturated and unsaturated hydrocarbons. For purposes of this invention, a non-iron catalyst may be used. The F-T catalyst may include a support, such as a metal-oxide support, including silica, alumina, silica-alumina or titanium oxides. For the purposes of this reaction, a Co catalyst on transition alumina with a surface area of approximately 100-200 m²/g is used in the form of spheres of 50-150 μm in diameter. The Co concentration on the support may also be 15-30%. Certain catalyst promoters and stabilizers may be used. The stabilizers include Group IIA or Group IIIB metals, while the promoters may include elements from Group VIII or Group VIIB. The Fischer-Tropsch catalyst and reaction conditions may be selected to be optimal for desired reaction products, such as for hydrocarbons of certain chain lengths or number of carbon atoms. Any of the following reactor configurations may be employed for Fischer-Tropsch synthesis: fixed bed, slurry reactor, ebullating bed, fluidizing bed, or continuously stirred tank reactor (CSTR). For the purposes of this reaction, a slurry bed reactor is used. The FTR may be operated at a pressure of 100 to 500 psia and a temperature of 375° F to 500° C. The reactor gas hourly space velocity ("GHSV") may be from 1000 to 8000 hr⁻¹. Syngas useful in

producing a Fischer-Tropsch product useful in the invention may contain gaseous hydrocarbons, hydrogen, carbon monoxide and nitrogen with H_2/CO ratios from about 1.8 to about 2.4. The hydrocarbon products derived from the Fischer-Tropsch reaction may range from methane (CH_4) to high molecular weight paraffinic waxes containing more than 100 carbon atoms. An overhead product stream is recovered from the FTR and may be separated into tail gas and light Fischer-Tropsch liquid ("LFTL") products in a cold separator. The LFTL stream may then be distilled to yield a hydrocarbon product of primarily C_{13} - C_{22} olefins and paraffins.

[22] The C_{13} - C_{22} distillation cut may be used directly as the base fluid. Low levels of C_{13} -hydrocarbons may be present in the C_{13} - C_{22} cut provided such levels do not cause the drilling fluid to exceed current regulatory limits. C_{13} -hydrocarbons may be present in amounts between about 0.01 and 10wt%. The presence of such small amounts of C_{13} -hydrocarbons permits incorporation of a wider distribution of C_{13+} hydrocarbons, particularly C_{16+} hydrocarbons, for improved lubricity. The hydrocarbon number distribution is such as to result in a drilling fluid pour point below about $10^\circ C$.

[23] Embodiments of the base fluid contains from about 5 to about 90wt% linear alpha- and internal olefins. The olefin content may provide the mixture with lower pour-point, better surface activity, better lubricity and better adherence to metal. When the base fluid is produced from the Fischer-Tropsch synthesis with the appropriate Fischer-Tropsch catalyst and operating conditions, the Fischer-Tropsch product will have approximately 5% alpha and internal olefin content. Depending upon the reaction conditions of the FTR and catalyst used in the Fischer-Tropsch reaction, it may be necessary to concentrate the olefin content to achieve the higher percentages of olefins in the base fluid. Concentration of olefins may be undertaken, for example, by one or more of the following known techniques: (1) molecular sieve separation of olefins and paraffins, such as UOP's OLEX[®] process, and (2) distillation of paraffins away from individual C_x cuts.

[24] The base fluid may contain between about 5 to about 95wt% paraffins. Of the total paraffin content from about 3 to about 20wt% are isoparaffins. Substantially all of the isoparaffins are terminal monomethyl species. As used herein, the terminal species include 2- and 3-methyl branched. The presence of monomethyl isoparaffins improves low temperature properties, such as pour point, as well as lubricity and viscosity. Moreover, because the

isoparaffins are predominantly terminally branched, the paraffin content of the base fluid is substantially wholly biodegradable. Using the Fischer-Tropsch synthesis described herein, about 5wt% terminal methyl branched paraffins are produced in the LFTL.

[25] Concentration of isoparaffins may be increased by one or more of the following techniques: (1) molecular sieve separation of linear and branched paraffins, such as UOP's OLEX[®] process, and (2) isomeric distillation of isoparaffin.

[26] Embodiments of the base fluid contain between about 0 and about 10 wt% oxygenates. The oxygenates are principally primary alcohols. Other oxygenates, including aldehydes, ketones, carboxylic acids and esters and di-esters of carboxylic acids are also present in small amounts. Oxygenate content in the C₁₃ - C₂₂ cut of the Fischer-Tropsch reaction product ranges from between about 0.5 to about 5.0wt%. Low levels of oxygenates in the drilling fluid from between about 0 and about 10wt% provide improved lubricity. Moreover, oxygenates may assist in emulsification in invert drilling muds.

[27] Oxygenate control may be used on the C₁₃-C₂₂ cut of the Fischer-Tropsch product stream. In one embodiment of the invention, a base fluid is produced by vaporizing a product stream and passing the vaporized product over an activated alumina catalysts to dehydrate alcohols to corresponding olefins. The conversion of the alcohol content of the product stream occurs according to the following reaction:



[28] For example, the LFTL, C₁₃-C₂₂ or other product stream may be vaporized at a temperature from about 400°F to about 800°F and then passed over one or more dehydration beds containing activated treated alumina or silica-alumina. In some embodiments, the dehydration beds are packed beds. Essentially all of the primary and internal alcohols present in the vaporized stream are dehydrated to their corresponding olefins, with conversion rates of at least 95%.

[29] Dehydration reaction temperature may range from between about 400° and 800°F. The vaporized feed for the dehydration unit may be superheated prior to being fed into the dehydration beds or alternatively, may be heated within packed beds. The LHSV of packed beds may range from about 0.10 hr⁻¹ to about 2.0 hr⁻¹. Reaction pressure may be maintained by the pressure of the accumulator and must be such to vaporize all of the dehydration feed. Typically, the pressure may range from between about 0 psia to about 100 psig.

[30] In an alternative embodiment, a moving bed of alumina or silica-alumina catalyst may be used. Fluidized beds, slurry beds or ebullating beds may be used with continuous batch or semi-batch catalyst removal and regeneration. The catalyst may be removed by one of these methods and regenerated by passing a mixture of nitrogen and oxygen or air at elevated temperatures over the catalyst.

[31] Depending upon the alumina used, some of the olefins present or produced in the dehydration beds may also be isomerized to internal olefins. Alumina catalysts useful for the dehydration of alcohols are known and include, for example, gamma-alumina, theta-alumina, pacified alumina, and activated alumina. High surface area aluminas are particularly useful in the invention and include those aluminas having a surface area of about 100 m²/gm or greater. Commercially available alumina useful in the integrated Fischer-Tropsch process include, for example, S-400, which has a surface area of about 335 m²/gm, and DD-470, which has a surface area of about 375 m²/gm. S-400 and DD-470 are alumina catalysts made and sold by Alcoa. Alumina catalysts for use in the integrated Fischer-Tropsch process generally contain at least about 90wt% Al₂O₃, oxides of silicon and iron present in amounts of less than about 0.1wt%, and oxides of sodium present in an amount of less than about 1 wt%. The alumina catalysts are generally supplied as substantially spherical particles having diameter from about 1/8 to about 1/4 inch.

[32] In another embodiment of the invention, molecular sieve or zeolitic molecular sieve forms of the alumina or silica-alumina catalysts may be used. For example, silico aluminophosphate ("SAPO") molecular sieves may be used in the packed beds. SAPO molecular sieves contain a 3-dimensional microporous crystal structure having 8, 10, or 12 membered ring structures. The ring structures can have an average pore size ranging from between about 3.5 angstroms to about 15 angstroms. Other silica-containing zeolitic molecular sieve catalysts, such as ZSM-5, may be used in the dehydration bed.

[33] Following dehydration, the aqueous and organic phases may be separated. Such dehydration process may further be used to increase the olefin content of the product stream to be used to produce the base fluid.

[34] Other methods of oxygenate control include, for example, reaction of the alcohol content of the C₁₃-C₂₂ cut of a Fischer-Tropsch product stream with maleic or succinic anhydride or with a carboxylic acid, such as formic acid, acetic acid, or other acids. The

carboxylic acid esters may be retained in the stream as they are excellent lubricants which are also highly biodegradable. Both the lubricity and the biodegradability of the base fluid may be improved by converting at least a portion of the alcoholic oxygenate content to carboxylic acid esters.

- 5 [35] The drilling fluid may optionally include one or more surfactants (e.g., emulsifiers, wetting agents), viscosifiers, weighting agents, fluid loss control agents, and proppants. Because the drilling fluid should be non-toxic, these optional ingredients, like the base fluid, are preferably also non-toxic. Acceptable emulsifiers include, but are not limited to, fatty acids, and fatty acid derivatives including amido-amines, polyamides, polyamines, esters, 10 imidaxiolines, and alcohols. Typical wetting agents include, but are not limited to, lecithin, fatty acids, crude tall oil, oxidized crude tall oil, organic phosphate esters, modified imidazolines, modified amidoamines, alkyl aromatic sulfates, alkyl aromatic sulfonates, and organic esters of polyhydric alcohols. Exemplary weighting agents include, but are not limited to, barite, iron oxide, gelana, siderite, calcium oxide, and calcium carbonate. Acceptable 15 proppants include sand, gravel, and nut shells. Exemplary viscosifiers include, but are not limited to, organophilic clays, non-organophilic clays, oil soluble polymers, polyamide resins, and polycarboxylic acids and soaps. Where additives are used in the drilling fluid, the base fluid constitutes from about 25 to about 85 volume percent of the total drilling fluid. Illustrative fluid loss control agents include, but are not limited to, asphaltics (e.g., asphaltenes and 20 sulfonated asphaltenes), modified lignites, and polymers, such as polystyrene, polybutadiene, polyethylene, polypropylene, polybutylene, polyisoprene, natural rubber, and butyl rubber.
- [36] The following examples illustrate, but are not intended to limit, the invention.

25 Example 1

[37] A pilot installation consisting of two distillation columns was used to produce C₆₋₁₀ naphtha, C₁₀₋₁₃ light kerosene, and C₁₃₋₂₀₊ drilling fluid feedstock streams. The columns were fed approximately 3400 g/hr of light Fischer Tropsch liquid (LFTL). The LFTL feed had approximately the composition shown in Table 1:

TABLE 1

Carbon #	% by wt.
4	<0.1
5	0.01
6	0.3
7	1.0
8	2.9
9	5.9
10	8.1
11	9.2
12	9.5
13	9.2
14	8.4
15	7.9
16	7.1
17	6.2
18	5.4
19	4.6
20	3.7
21	3.0
22	2.3
23	1.7
24	1.2
25+	2.6
Total	100.00

[38] The LFTL feed was introduced into a first packed distillation column and C₁₃ and lighter materials were distilled overhead. The first distillation column was operated at the following conditions: 10 psig, 480°F feed preheat temperature, 407°F overhead temperature, 582°F bottoms temperature. The first distillation column had approximately 98 inches of Sulzer Mellapack 750Y packing. The bottoms of the first distillation column constituted a C₁₃-20+ hydrocarbon fraction, the composition of which is shown in Table 2. The overhead stream of the first distillation column was fed into a second packed distillation column operated at 12 psig, 370°F overhead temperature and 437°F bottoms temperature. The second distillation column had about 28 inches of Sulzer EX packing. The bottoms of the second column constituted a C₁₀₋₁₃ light kerosene stream.

TABLE 2

Total n-paraffins, isoparaffins, olefins and alcohols		
C ₁₁ :-	Mass%	0.97
C ₁₂ :-	Mass%	1.77
C ₁₃ :-	Mass%	11.43
C ₁₄ :-	Mass%	13.68
C ₁₅ :-	Mass%	12.35
C ₁₆ :-	Mass%	10.96
C ₁₇ :-	Mass%	9.06
C ₁₈ :-	Mass%	7.84
C ₁₉ :-	Mass%	6.79
C ₂₀ :-	Mass%	7.04
C ₂₁ :-	Mass%	5.66
C ₂₂ :-	Mass%	4.63
C ₂₃₊ :-	Mass%	7.83
		100.00

Example 2

[39] The C₁₃₋₂₀ and stream from Example 1 was fed via a syringe pump and mixed with 20 cc/min of nitrogen. The gas/liquid mixture was introduced upflow into a vessel packed with stainless steel mesh saddles, where the liquid was vaporized and superheated to reaction temperature of 675°F. The vaporized feed was fed upflow into a reactor packed with 1/8 Alcoa S-400 alumina catalyst and suspended in a heated sandbath. The sandbath was maintained at the reaction temperature and ebulated by air. Reactor LHSV was maintained at about 0.26 hr⁻¹. The outlet pressure was maintained at about 5 psig. The reaction product composition is shown in Table 3.

TABLE 4

Sample Reference Number		FEED B	PRODUCT D
TOTAL			
N-PARAFFIN	mass %	82.46	82.87
ALPHA OLEFIN	mass %	2.26	3.48
INTERNAL OLEFIN	mass %	2.75	3.68
BRANCHED PARAFFIN	mass %	10.10	9.97
ALCOHOL	mass %	2.45	0.00
		100.00	100.00

Example 3

[40] An LFTL feed, substantially having the composition shown in Table 1, was hydrotreated at reactor conditions of 800 psig and 550° to 590°F. The resulting hydrotreated

stream was distilled under conditions as described in Example 1 forming a hydrotreated analog of the C₁₀-C₁₃ light kerosene product. This hydrotreated light kerosene material was analyzed on a Hewlett Packard Series II gas chromatograph with 60 m RTX 1 column with 0.32 mm diameter and 3 micron film thickness. The isomer content of this product is shown in Table 4.

5

TABLE 5

Component	Wt. %
nC ₉ -	0.02
2- and 3-monomethyl C ₁₀	0.20
4- and higher – monomethyl C ₁₀	0.03
nC ₁₀	22.22
2- and 3-monomethyl C ₁₁	1.19
4- and higher – monomethyl C ₁₁	0.42
nC ₁₁	27.93
2- and 3-monomethyl C ₁₂	1.09
4- and higher – monomethyl C ₁₂	0.50
nC ₁₂	24.96
2- and 3-monomethyl C ₁₃	0.92
4- and higher – monomethyl C ₁₃	0.48
nC ₁₃	18.99
2- and 3-monomethyl C ₁₄	0.11
4- and higher – monomethyl C ₁₄	0.13
nC ₁₄	0.41
Total normal hydrocarbon	94.54
Total 2- and 3- monomethyl substituted hydrocarbons	3.51
Total 4- and higher – monomethyl substituted hydrocarbons	1.55
Total monomethyl hydrocarbons	99.61
Others	0.39

[41] While the foregoing describes preferred embodiments of the invention, it is apparent that a number of changes and variations are within the scope and spirit of the invention.

10 [42] What is claimed is: